Oxygen Nonstoichiometry and Electronic Conduction Mechanism of Layered Perovskite-Type Oxides

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論 文 内 容 要 旨

The purpose of this study is establishing a comprehensive model for physical properties which will be a guidepost for material researches on functional materials. Toward this aim, the author choose layered perovskite-type oxides, $Ln_{2-x}Sr_xNiO_{4+\delta}$ (Ln = La, Nd) as a functional inorganic crystalline material. Oxygen nonstoichiometry, electronic state, and crystal structure of Ni-based K_2NiF_4-type oxides are systematically examined (Chapter 2-5). The relationship between these physical properties is discussed by solid-state chemical and solid-state physical methods. As a prototype of comprehensive model, defect equilibrium and statistical thermodynamic models are proposed in chapter 4, conduction mechanism and band structure are illustrated in Chapter 3, and the effects of structural variation on nonstoichiometric behavior and band structure are clearly illustrated in chapter 5.

General introduction of this work is written in Chapter 1. After the relation between innovation of technologies and material development is mentioned, strategies of material developments are briefly summarized. As a typical strategy for material development of inorganic materials, enhancing functionalities, discovering new functionality, reducing environmental burden, cost reduction, and stable supply of raw materials are introduced. The author chose Ni-based K_2NiF_4-type oxides as a target material of this study because this system shows interesting properties in both industrial and scientific point of view. The former works including both solid-state physical and solid-state chemical studies are briefly summarized. The biggest issue is that the inconsistency of physical and chemical works. The combination of oxygen nonstoichiometry, electronic conduction mechanism, and crystal structure is to be a good example of the combination of solid-state physical and solid-state chemical knowledge. Finally, the aim of this study and subsequent spreading effects are shown with schematic pictures.

In Chapter 2, oxygen nonstoichiometric behavior of $Ln_{2-x}Sr_xNiO_{4+\delta}$ (Ln = La, Nd) are investigated. Because the variation of oxygen content from stoichiometric composition affects both electronic and electrochemical properties, the basic information of oxygen content is essential for the fair research. La-series and Nd-series K_2NiF_4-type oxides show both oxygen excess and oxygen deficient compositions depending on temperature, $P(O_2)$, and the Sr content. As the Sr content increases, the oxygen excess region decreases and the oxygen deficient region increases. At given conditions, i.e., at the same T, $P(O_2)$ and x, the amount of excess

oxygen of $Nd_{2-x}Sr_xNiO_{4+\delta}$ is larger than that of $La_{2-x}Sr_xNiO_{4+\delta}$, while the nonstoichiometric behavior in the oxygen deficient region is almost the same. This may be caused by the structural difference in the rock salt layer where interstitial oxygen is located. Partial molar enthalpy and partial molar entropy of oxygen are calculated by the Gibbs-Helmholtz equation with measured nonstoichiometric data. As the interstitial oxygen increases, partial molar enthalpy of oxygen approaches zero in the oxygen excess region, while that is independent of δ in the oxygen deficient region. This means that the system behaves as an ideal solution system does in the oxygen deficient region, and deviates from the ideal-solution-like state in the oxygen excess region. As the amount of excess oxygen increases, interstitial oxygen formation is suppressed in $Ln_{2-x}Sr_xNiO_{4+\delta}$. Compared to $Nd_{2-x}Sr_xNiO_{4+\delta}$, the variation of partial molar enthalpy of oxygen with δ in oxygen excess region is larger in $La_{2-x}Sr_xNiO_{4+\delta}$. This means that the oxygen nonstoichiometric behavior of $Nd_{2-x}Sr_xNiO_{4+\delta}$ is more ideal-solution-like than that of $La_{2-x}Sr_xNiO_{4+\delta}$. Decomposition $P(O_2)$ for $Ln_{2-x}Sr_xNiO_{4+\delta}$ is independent of the Sr content, and similar to that for NiO. Decomposition $P(O_2)$ for non-doped $La_2NiO_{4+\delta}$ and $Nd_2NiO_{4+\delta}$ shows discrepancy depending on the thermal history. The equilibrium potential at the decomposition point measured with elevating temperature after the oxygen extraction at 873 K is different from that measured with lowering temperature after the oxygen extraction at 1173 K. The gap becomes large as temperature decreases. The gap of decomposition $P(O_2)$ for $La_2NiO_{4+\delta}$ at 873 to 1173 K extends the gap of decomposition $P(O_2)$ reported by former works.

In Chapter 3, the electronic state and conduction mechanism of $Ln_{2-x}Sr_xNiO_{4+\delta}$ (Ln = La, Nd) at high temperatures are discussed based on the multilateral evaluation by combining oxygen nonstoichiometric data (shown in Chapter 2), electronic conductivity, and thermoelectric voltage. The polarity of thermoelectric voltage indicates that the electronic carrier of Ni-based K_2NiF_4-type oxides is positive holes in the temperature range between 573 and 1173 K and $P(O_2)$ range between 1 and 1×10^{-4} bar. Electronic conductivity increases with temperature in the lower temperature region as in semiconductors, while that decreases as temperature increases in the higher temperature region as in metals. Apparent metal-semiconductor transition was confirmed at around 600 K as many earlier work reported. Hole mobility was calculated from the electronic conductivity and the hole concentration which is proportional to the sum of the Sr content and nonstoichiometric oxygen content. In the lower temperature region, hole mobility is thermally activated as in semiconductors, and hole mobility slightly decreases as temperature increases as in metals in the higher temperature region. This behavior strongly indicates delocalized electronic state in the higher temperature region. The conduction mechanism of $Ln_{2-x}Sr_xNiO_{4+\delta}$ was studied using the theoretical equation of Seebeck coefficient for metallic conductors, semiconductors, and hopping conduction materials (localized systems). Only the metallic conductor model can explain the relationship between Q, σ, and p. Besides the temperature dependence of the hole mobility, the relationship between Q, σ, and p also indicate p-type metal like band conduction of $Ln_{2-x}Sr_xNiO_{4+\delta}$ (Ln = La, Nd) at high temperatures. Density of states is calculated from the relationship between Q, σ, and p. It is found that the rigid-band-like state is maintained in Ni-based K_2NiF_4-type oxides, i.e., the density of states is independent of the Sr content and the amount of oxygen nonstoichiometry. The band structure for $Ln_{2-x}Sr_xNiO_{4+\delta}$ is proposed based on the experimental results and former solid-state physical studies. Free holes in the $\sigma_{x2-y2}\uparrow$ band contribute the p-type metallic conduction of $Ln_{2-x}Sr_xNiO_{4+\delta}$ at high temperature region.

In Chapter 4, defect chemical and statistical thermodynamic analyses are made on to determine defect formation mechanism and the relation between defect species and thermodynamic quantities of $Ln_{2-x}Sr_xNiO_{4+\delta}$. To reflect the results in Chapter 2 and 3 on the defect equilibrium model, several modifications are introduced in the model. The deviation from ideal-solution-like state is expressed by the excess enthalpy which is assumed to be proportional to δ. Because p-type metallic state is maintained in

$Ln_{2-x}Sr_xNiO_{4+\delta}$ at high temperatures, chemical potential of holes is directly derived from the analytical solution of the integration of the Fermi-Dirac distribution function and the density of states for two-dimensional conductors instead of the conventional Boltzmann approximation form. Proposed defect equilibrium model can well explain the nonstoichiometric behavior of Ni-based K_2NiF_4-type oxides. From the results of model fitting, similarities and differences in nonstoichiometric behavior between La-series and Nd-series K_2NiF_4-type oxides are discussed. To make theoretical relationship between defect species and thermodynamic quantities, partial molar enthalpy of oxygen and partial molar entropy of oxygen, statistical thermodynamic model is theoretically derived from the differentiation of Gibbs free energy of the system with respect to oxygen content. Partial molar quantities can be expressed by the product of defect species and Gibbs free energy change of the interstitial oxygen formation and oxygen vacancy formation. Calculated results agree with thermodynamic quantities determined from the δ-T-$P(O_2)$ relationship. The union of solid-state physics and solid-state chemistry is well demonstrated by the model shown here.

In Chapter 5, structural information of $La_{2-x}Sr_xNiO_{4+\delta}$ and $Nd_{2-x}Sr_xNiO_{4+\delta}$ under controlled T and $P(O_2)$ are shown, which is measured by high temperature X-ray diffraction measurements in N_2-O_2 atmosphere at 873-1173 K. Obtained diffraction patterns of $Ln_{2-x}Sr_xNiO_{4+\delta}$ can be indexed by a tetragonal symmetry except for that of $Nd_2NiO_{4+\delta}$ at 873 K in O_2 which is indexed by an orthorhombic symmetry. Orthorhombic-Tetragonal phase transition was observed in $Nd_2NiO_{4+\delta}$. Temperature vs. oxygen content phase diagram is illustrated from the relationship between temperature, oxygen content, and phase transition points. Rietveld analysis was made on the diffraction patterns to obtain the structural parameters' information. As the amount of excess oxygen increases, the lattice parameter perpendicular to the perovskite and rock salt layers increases and that parallel to the layers slightly decrease. As a result, the cell volume is almost independent of the excess oxygen content. Total differential equation of the lattice parameter with a linear approximation can explain the variation of the lattice parameters with T and δ. Thermal expansion coefficient and chemical expansion coefficient were calculated and compared with other nonstoichiometric compounds. The space in the rock salt layer and the lattice parameter perpendicular to the rock salt and perovskite layers essentially depend on the acceptor concentration, while the lattice parameter parallel to the layers mainly vary with x. Plausible explanation for these results is that the structure of the rock salt layer is essentially determined by the acceptor concentration. The space in the rock salt layer decreases as the acceptor concentration increases in $La_{2-x}Sr_xNiO_{4+\delta}$, while the space in the rock salt layer is almost independent of the acceptor concentration in $Nd_{2-x}Sr_xNiO_{4+\delta}$. This indicates that the interstitial oxygen formation is suppressed as the acceptor concentration increases in $La_{2-x}Sr_xNiO_{4+\delta}$, and the suppression effect is more significant in $La_{2-x}Sr_xNiO_{4+\delta}$ than $Nd_{2-x}Sr_xNiO_{4+\delta}$. The structural parameters' change revealed in this study is qualitatively consistent with our former works of nonstoichiometric behavior and the electronic structure on $Ln_{2-x}Sr_xNiO_{4+\delta}$ at high temperatures.

Through the work in this thesis, the relationship between oxygen nonstoichiometry, electronic state, and crystal structure of Ni-based K_2NiF_4-type oxides is successfully determined. The author applied both solid state chemical and solid state physical approaches to fairly understand the nature of Ni-based K_2NiF_4-type oxides. Although further work is necessary to obtain deeper understanding about the origin and the mechanism of functionality, the author is confident that the results shown in this thesis contribute to both scientific researches and industrial fields. From the industrial point of view, this thesis advance the electrochemical and electronic devices composed of Ni-based K_2NiF_4-type, and from the scientific point of view, the author demonstrate the combination of the solid-state physical and solid-state chemical methods. Methodology and techniques used in this study are also valid to examine other functional materials.

論文審査結果の要旨

多くの遷移金属酸化物では，遷移金属イオンの複数の原子価状態が共存し得るため，雰囲気が酸化性から還元性まで様々に変化するのに伴って遷移金属イオンの平均原子価が連続的に変化する．それと同時に酸化物中の酸素量が連続的に変化し，酸素不定比組成が生じる。これは酸化物の結晶格子の大きさや歪みに変化をもたらし，電子的性質や機械的性質にも大きな影響を与えると考えられる。酸素不定比組成－物性－構造の相互関係は材料機能設計にとって極めて重要である。しかし，この関係を実験と理論の両面から検証した例は未だ殆どない。一方，層状ペロブスカイト型構造を有する希土類 Ln とストロンチウム Sr およびニッケル Ni の複酸化物，組成式 $Ln_{2-x}Sr_xNiO_{4+d}$，は高温型燃料電池の電極や酸素透過膜の材料であり，強相関電子系の物性論においても重要であるため，基礎的知見へのニーズは高い。

本論文は，酸素不定比組成－物性－構造の相互関係を明らかにする研究体系の構築を目的とし，ニッケル系層状ペロブスカイト酸化物の内，希土類元素がランタンとネオジウムである２系について各々ストロンチウム含有量が異なる５種類の組成に関する 600-900℃での実験と，格子欠陥および電子構造のモデル構築とを通じて上記関係を解明したもので，全編６章からなる。

第１章は序論であり，本研究の背景，目的及び構成を述べている。

第２章では，雰囲気制御高温微重量天秤と高温固体電池による電量滴定法とを用いて，酸素含有量を温度，酸素分圧の関数として計測し，取り上げた系の不定比組成と酸素化学ポテンシャルなどの熱力学量との関係を明らかにしている。この系の重要な基礎データであり，既に学会発表等で内外数グループにより引用され始めている。

第３章では，上記の系について高温雰囲気制御下での導電率と熱起電力を計測し，酸素不定比量から求めたニッケルの価電子の数と導電率，熱起電力との関係を解析することにより，本系の高温での高い導電性が遍歴電子に由来することを明らかにしている。高温電子材料への応用という立場からも電子物性論の立場からも重要な知見である。

第４章では，電子系が金属的な挙動をし，イオン欠陥は正則溶液的に振る舞うという格子統計モデルを考案し，そのモデルによる数値計算が２章で得られた実験結果を完全に再現することを明らかにしている。材料の設計とシミュレーションに関わる重要な成果である。

第５章では，雰囲気制御高温Ｘ線回折装置により求めた結晶構造と不定比組成・温度との関係を述べている。組成一定のときの格子体積の温度変化，いわゆる熱膨張，と一定温度で不定比組成が変化したときの体積変化，いわゆる還元膨張，を分離計測することに成功し，さらにニッケルの電子状態と格子体積，格子定数との関係に議論を進めている。材料の機械的安定性確保という実用面からも，３章の結果とあわせて電子物性の本質に迫る基礎を与えることからも，貴重な知見である。

第６章は，結論である。

以上要するに本論文は，ニッケル系層状ペロブスカイト型酸化物を例に，熱力学・欠陥平衡論，物性物理学，結晶構造解析を総合した高温材料評価手法の雛形を提示したものであり，機械システムデザイン工学と固体イオニクスの発展に寄与するところが少なくない。よって，本論文は博士(工学)の学位論文として合格と認める。